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Taming the germyliumylidene $[ClGe:]^+$ and germathionium $[ClGe{=}S]^+$ ions by donor–acceptor stabilization using 1,8-bis(tributylphosphazenyl)naphthalene†

Yun Xiong, Shenglai Yao, Shigeyoshi Inoue, Andreas Berkefeld and Matthias Driess*

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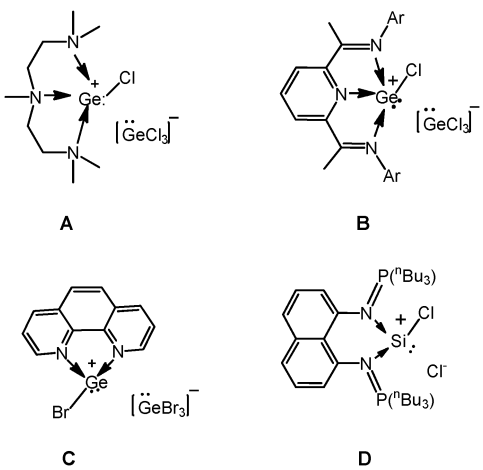
The novel chlorogermyliumylidene complex $L[ClGe:]^+$ (L = 1,8-bis(tri-*n*-butylphosphanzenyl)naphthalene) with a 'naked' Cl^- as a counter anion was synthesized through reaction of L with $Cl_2Ge:$ and fully characterized. Its reaction with elemental sulfur afforded the first germathionium $[ClGe{=}S]^+$ cation containing species. The latter has also been fully characterized, including single-crystal X-ray diffraction analysis.

Germyliumylidenes $RGe:^+$, that is, monocations of divalent germanium, which possess an ambiphilic nature as both Lewis bases and acids, have received increasing attention during the last decade. $RGe:^+$ species with mono-coordinating groups R and without further coordinating neutral ligands have never been isolated owing to their poor stability. To date, with poly-coordinating groups R or with additional neutral ligands a series of higher coordinated $RGe:^+$ species were obtained, although the character of the respective $RGe:^+$ is drastically changed. The first germyliumylidene containing species $[(Me_5C_5)Ge:]^+[BF_4]^-$ was obtained by Jutzi and co-workers through protonation of the divalent germanium compound $(Me_5C_5)_2Ge:$ using HBF_4 as a proton source.[1] By analogy, the protonation of the germylene $\{[CH(NAr)]_2Ge:\}$ with $[H(OEt_2)_2][B(C_6F_5)_4]$ allowed Müller and co-workers to isolate the germyliumylidene species $[ArN{=}CH{-}CH_2N(Ar)(Et_2O)Ge:]^+[B(C_6F_5)_4]^-$ (Ar = 2,6-*i*$Pr_2C_6H_3$) in 2009.[2] Recently, the groups of Reid and Roesky realized that through auto-ionization of $:GeX_2$ (X = Cl, Br), mediated by Lewis bases such as neutral bi-, or tri-dentate ligands, certain germyliumylidenes containing ion pairs $[RXGe:]^+[:GeX_3]^-$ (R = organic bi- or tridentate ligands) could be prepared (Scheme 1, **A–C**).[3,4] Furthermore, by employing multi-dentate ligands such as crown ethers or cryptands, results from Baines and co-workers showed that even Ge^{2+} complexes can result in the form of $[(\text{crown ether})Ge:]^{2+}$ $2[:GeX_3]^-$ ion triples, depending on the nature of the multi-dentate donor ligands.[5a,b] Similarly, by using [2.2.2]paracyclophane ($C_{24}H_{24}$) as a π-donor ligand L and $AlCl_3$ as an acceptor of Cl^- under partial hydrolysis conditions the peculiar Ge(II) species $[L(Cl)Ge:]_2^+[Al_4O_2Cl_{10}]^{2-}$ could be isolated by Schmidbaur and co-workers.[6] On the other hand, it is noteworthy that if triflate OTf^- ($OSO_2CF_3^-$) was introduced into the reaction involving crown ethers or cryptand ligands, simple Cl/OTf^- anion exchange instead of auto-ionization takes place, yielding the similar germyliumylidene complexes with triflate anion rather than formation of the $[GeX_2(OTf)]^-$ anions as counter ions.[5a,b] Likewise, a remarkably new type of monoamido-germyliumylidene complexes with weak intramolecular arene stabilization could be prepared by Jones, Krossing and co-workers.[5c]

Recently, we have shown that a bis-phosphorus ylide can serve as an efficient donor shell to stabilize even highly Lewis-acidic Si(II) sites.[7] The striking ability of ylide-like ligands to stabilize low-valent Si cations was further demonstrated by using the bidentate 1,8-bis(tri-*n*-butylphosphazenyl)naphthalene ligand which can even substitute the *N*-heterocyclic carbene (NHC) and a chloride ligand of NHC-$SiCl_2$ (NHC = 1,3-bis(2,6-diisopropylphenyl)-4,5-imidazol-2-ylidene) to form the first chlorosilyliumylidene chloride complex **D** (Scheme 1).[8] Unexpectedly, no auto-ionization reaction as mentioned above was observed. The straightforward synthesis of **D** prompted us to examine the reactivity of 1,8-bis(tri-*n*-butylphosphazenyl)-naphthalene towards $GeCl_2$·dioxane. Herein we report the



Scheme 1 The germyliumylidenes **A–C** and the silyliumylidene complex **D**.

Technische Universität Berlin, Department of Chemistry, Metalorganics and Inorganic Materials, Sekr. C2, Strasse des 17. Juni 135, D-10623 Berlin, Germany. E-mail: matthias.driess@tu-berlin.de, http://www.driess.tu-berlin.de; Fax: +49 30-314-29732

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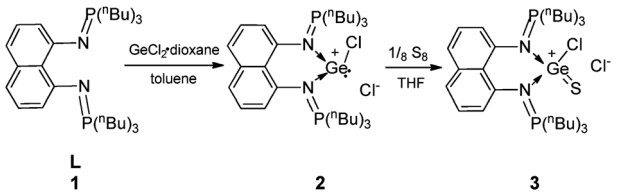


Scheme 2 Synthesis of the chlorogermyliumylidene chloride complex **2** and its oxidation to give the chlorogermathionium salt **3**.

synthesis and structural characterisation of the germanium analogue of **D** and its oxidation reaction with elemental sulfur to form the first $[ClGe{=}S]^+$ cation containing species.

When an equimolar amount of $GeCl_2$·dioxane was added into a solution of 1,8-bis(tri-*n*-butylphosphazenyl)naphthalene **L** (**1**) in toluene at ambient temperature, a precipitate formed immediately, indicating the formation of the desired ionic species **2** (Scheme 2). After work-up, complex **2** could be isolated as white powder in moderate yield (60%). Both ESI-MS and EI-MS spectrometric investigations of **2**, similar to **D**, gave only the molecular ions of the free ligand **L**. However, the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra, elemental analysis and single crystal X-ray diffraction analysis confirmed that **2** represents the ion pair $[\mathbf{L}(Cl)Ge{:}]^+Cl^-$ (Scheme 2).

The ^{31}P NMR spectrum of **2** shows a singlet at δ 55.1 ppm, giving only about 3 ppm up-field shift compared with that of **D** (δ 57.7 ppm).[8] Colorless crystals of **2** suitable for X-ray diffraction analysis were grown in THF at −20 °C. The compound crystallizes in the monoclinic space group $P2_1/n$. As expected, the germanium atom is three-coordinated by one chlorido ligand and two nitrogen atoms of the bis-phosphazenyl ligand **L** (Fig. 1). The second Cl^- as a counter anion is located far away from the germanium atom with the closest Ge···Cl distance of 6.752 Å. The six-membered C_3N_2Ge ring in the cation of **2** is puckered with the germanium atom out of the plane defined by the C_3N_2 atoms. The Ge–Cl bond is oriented nearly perpendicular to both two N–Ge bonds with bond angles of 95.4(1)° for N1–Ge1–Cl1 and 96.2(1)° for N2–Ge1–Cl1. The Ge–Cl distance of 2.278(1) Å in **2** is in agreement with the Ge–Cl distance in **A** (2.266(2) Å)[3] and in **B** (2.243(1) Å).[4] Both Ge–N bond distances of 1.981(3) Å and 1.960(3) Å in **2** are, however, slightly shorter than those in **A** (2.114(5)–2.428(5) Å)[3]

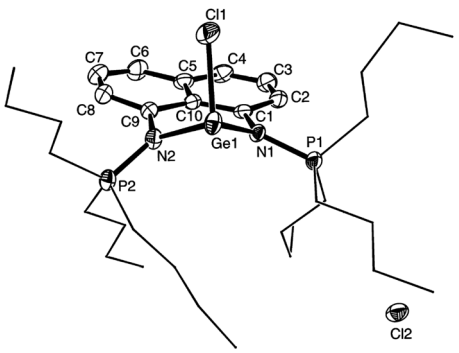


Fig. 1 Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and one THF molecule are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1–N1 1.981(3), Ge1–N2 1.960(3), Ge1–Cl1 2.278(1), P1–N1 1.653(3), P2–N2 1.640(3); N1–Ge1–N2 88.3(1), N1–Ge1–Cl1 95.4(1), N2–Ge1–Cl1 96.2(1).

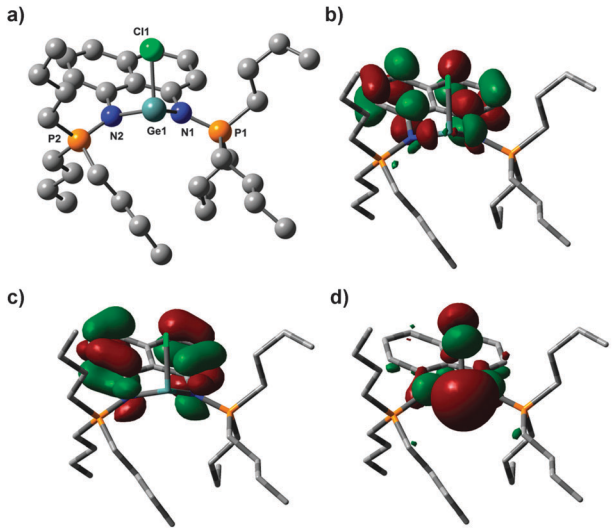


Fig. 2 (a) Calculated structure of the cation in **2** (B3LYP/6-31G(d) level). Calculated molecular orbitals of the cation in **2**: (b) LUMO (−0.1288 eV), (c) HOMO (−0.2839 eV), (d) HOMO − 1 (−0.3145 eV). Hydrogen atoms are omitted for clarity.

and in **B** (2.071(2)–2.267(2) Å),[4] indicating the stronger interaction between the N atoms and the Ge atom in **2** than those in **A** and **B**. Complex **2** is isostructural with the silicon analogue **D** and the P–N distances (1.653(3), 1.640(3) Å) in **2** are very close to those observed in **D** (1.666(3), 1.659(3) Å).[8] The latter P–N distances lie between those of P–N single (1.75–1.80 Å)[9] and double bonds (1.51–1.57 Å),[10] exhibiting the delocalization of the positive charge in the cation of **2** in both P=N ylide moieties.

In order to gain further insight into the electronic structure of the cation **2**, quantum-chemical calculations (B3LYP/6-31G(d)) were carried out (see ESI†). The geometry optimization of the 'naked' cation in **2** revealed a structure close to that observed experimentally (Fig. 2a). While the LUMO of **2** consists mainly of the naphthalene π-system (Fig. 2b), the HOMO of **2** represents a π-bonding orbital comprised of the 10 π-electron naphthalene moiety and the lone pairs at the nitrogen atoms of the P–N ylide groups (Fig. 2c). The lone pair orbital at Ge atom is clearly dominating in the HOMO − 1 (Fig. 2d). Similar to silicon analogue **D**, the energy difference between the HOMO and HOMO − 1 is strikingly small (*ca.* 0.03 eV), suggesting an interesting reactivity on the naphthalene system as well as at the Ge(II) atom. The NPA (Natural Population Analysis) showed that each P atom in the P–N ylide moieties has a large positive net charge (+1.907 and +1.908), while the N atoms bear negative charges (−1.161 and −1.169), like in silicon derivative **D**. The positive charge of the Ge atom was also supported by NPA (+0.964). Furthermore, the WBI (Wiberg Bond Index) values of the P–N (0.919 and 0.922) and the Ge–N bonds (0.436 and 0.430) display ylide and dative bond character, respectively. Thus, due to the intriguing ylide resonance stabilization, the cation in **2** possesses similar resonance structures as silyliumylidene **D**.[8]

Compound **2** represents a novel stable Ge(II) cation complex with merely Cl^- as a counter ion. In contrast to the transformation of [(2,2′-bipy)$GeBr_2$] to $[(2,2'\text{-bipy})BrGe{:}]^+[GeBr_3]^-$(bipy = bipyridine) in solutions (Scheme 1, **C**),[3] the corresponding

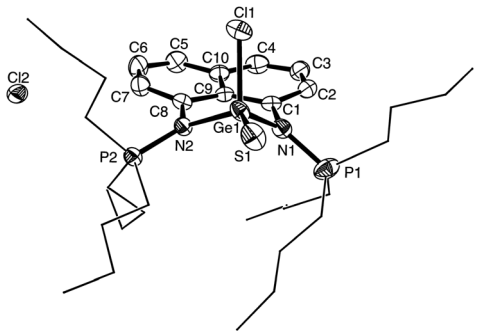
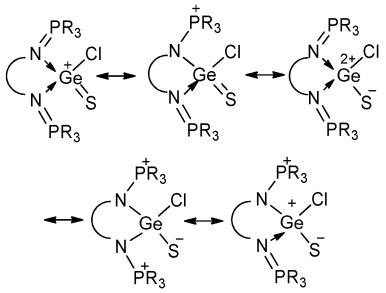


Fig. 3 Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and one THF molecule are omitted for clarity. Selected bond distances (Å) and angles (°): Ge1–N1 1.897(4), Ge1–N2 1.900(3), Ge1–Cl1 2.181(1), Ge1–S1 2.066(1), P1–N1 1.666(4), P2–N2 1.669(3); N1–Ge1–N2 93.0(2), N1–Ge1–S1 120.9(1), N2–Ge1–S1 123.6(1).



Scheme 3 Resonance structures of the cation in **3**.

conversion of **2** to [**L**(Cl)Ge:][$GeCl_3$]$^-$ could not be detected. However, when equimolar amount of $GeCl_2$·dioxane was added to a solution of **2** in THF, the counter ion Cl^- in **2** is captured by $GeCl_2$ to give the corresponding [$GeCl_3$] salt, which was confirmed by electrospray-MS spectrometry (negative mode) and ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (see ESI†). Accordingly, the reaction of **L** with $GeCl_2$·dioxane in the molar ratio of 1 : 2 in THF leads exclusively to [**L**(Cl)Ge:]$^+$[$GeCl_3$]$^-$.

Similar to **D**, complex **2** can react with elemental sulfur in THF at ambient temperature to furnish the first germathionium [ClGe═S]$^+$ cation containing species **3** in the form of pale yellow crystals in 40% yield (Scheme 2). Compound **3** shows a singlet at δ 65.3 ppm in the ^{31}P NMR spectrum, giving a down-field shift of *ca.* 11 ppm compared with that of its precursor **2** (δ 55.1 ppm). The latter value is very close to that of the corresponding silathionium containing species (δ 65.9 ppm).[8] Its molecular structure was elucidated by single-crystal X-ray diffraction analysis (Fig. 3).

Complex **3** crystallizes in the monoclinic space group $P2_1/c$. The ion pair comprises of a ligand stabilized germathionium cation and a non-coordinating naked chloride anion. The germanium atom is now tetrahedrally coordinated by two nitrogen atoms from the bidentate ligand, one chloride and one terminal sulfur atom. The chloride counter anion is located far away from the germanium atom with the closest Ge···Cl distance of 6.834 Å. In comparison with the structure of the cation in **2**, the six-membered C_3N_2Ge ring in **3**, owing to the tetrahedral coordination of the germanium atom, is more strongly puckered with a larger dihedral angle of 48° (*vs.* 40° in **2**) between the planes defined by C_3N_2 and N_2Ge. Owing to the oxidation of the germanium atom from +II to +IV, compound **3** shows shortening of the Ge–Cl distance (2.181(1) Å *vs.* 2.278(1) Å in **2**) inspite of the increase of the coordination number of the germanium atom. The same is true for the mean Ge–N distance (1.899 Å) in **3** compared with that in **2** (1.971 Å). The Ge–S bond distance (2.066(1) Å) in **3** is close to those of Ge═S bonds stabilized by an intramolecular donor (ranging from 2.049(3) Å to 2.063(3) Å),[11–13] but shorter than the reported Ge–S single bond distance (2.239(1) Å),[14] implying the ylide nature of the Ge═S moiety as depicted in Scheme 3. Similarly, the mean P–N distance of 1.668 Å in **3** lies between those of the P–N single bonds (1.75–1.80 Å)[9] and P═N double bonds (1.51–1.57 Å),[10] reflecting also the ylide nature of the P═N moieties. Presumably, the combination of such resonance stabilisation enables the isolation of the elusive chlorogermathionium cation [ClGe═S]$^+$ as a complex.

In summary, the neutral bidentate bis-ylide ligand **1** shows extremely strong coordination ability in the reaction with the $GeCl_2$·dioxane complex. Through ligand exchange reaction instead of auto-ionization it enabled the synthesis of the first isolable chlorogermyliumylidene chloride complex **2** with a 'naked' chloride as a counter ion. The latter complex allowed the facile oxidation of the Ge(II) atom in **2** by elemental sulfur to afford the first chlorogermathionium cation containing species **3** bearing a terminal Ge═S subunit.

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